WASTES IN PRODUCTION

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USE OF WASTES FROM CONCENTRATION OF ALKALI SYENITES FROM THE ELET'OZERSKOE DEPOSIT FOR MANUFACTURE OF CERAMIC TILES

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The effect of the mineralogical composition of wastes from concentration of alkali syenites on the structure and properties of ceramic tile was established. The ceramics obtained after firing at 950 – 1100°C have an irregularly granular structure consisting of a fine-grained base (grain size less than 5 μm) and disseminated deposits 10 – 50 μm (in ceramics with slurry) and up to 120 μm (in ceramics with a magnetic fraction) in size. The glass phase is enriched with aluminum, magnesium, and iron oxides contained in syenite concentration wastes and has an inhomogeneous chemical composition. It was shown that the higher content of iron minerals in the magnetic fraction in comparison to slurry significantly intensifies glass formation and sintering of the ceramic, causing low water absorption and high strength.

Key words: alkali syenites, concentration wastes, raw material, sintering, ceramic tile.

Ceramic facing materials are increasingly widely used in construction. Low-melting polymineral, basically hydromica clays are used to manufacture them, and natural materials and mining industry wastes are used as additives that improve the properties of the articles. Since such additives usually consist of several minerals, their effect on the structure and properties of the ceramics must be investigated.

Alkali syenites in the Elet'ozerskoe massif occupy an area of approximately 15 km^2. Syenites from the Northern section have been most investigated. The rocks in the Northern section consist of 73 – 84% alkali feldspars (microcline, albite), nepheline (1.2 – 1.5%), magnesium iron silicates (biotite, alkali amphibole, pyroxene), and accessory minerals (apatite, magnetite, sphene, fluorite) [1].

A scheme for concentration of the raw material was developed at IG KarNTs RAN and an experimental lot of nepheline-feldspar concentrate was obtained (0.3% Fe_2O_3 content[2]). The high alkali oxide content allowed using the concentrates as flux in sanitary and industrial ceramics. Studies of the concentrate in production conditions showed its suitability for production of ceramic granite facing and façade tiles.

In concentration of syenites, 44 – 48% waste is formed, including a magnetic fraction (grain size < 0.5 mm) and a slurry fraction (particle size < 0.1 mm) formed in obtaining concentrates [1, 2].

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[2] Here and below — content by weight.

TABLE 1. Chemical Composition of Clay and Fillers

Raw material	Mass content, %											
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O	other
Slurry	54.56	0.80	18.63	2.67	4.24	0.20	1.38	3.37	6.50	5.62	0.10	1.67
Magnetic fraction	46.15	2.60	12.33	7.00	12.12	0.63	2.50	6.71	4.12	4.34	0.27	1.12
Chekalovskoe clay	62.70	0.85	15.45	3.24	2.70	0.03	2.50	0.97	0.21	5.19	1.11	4.46

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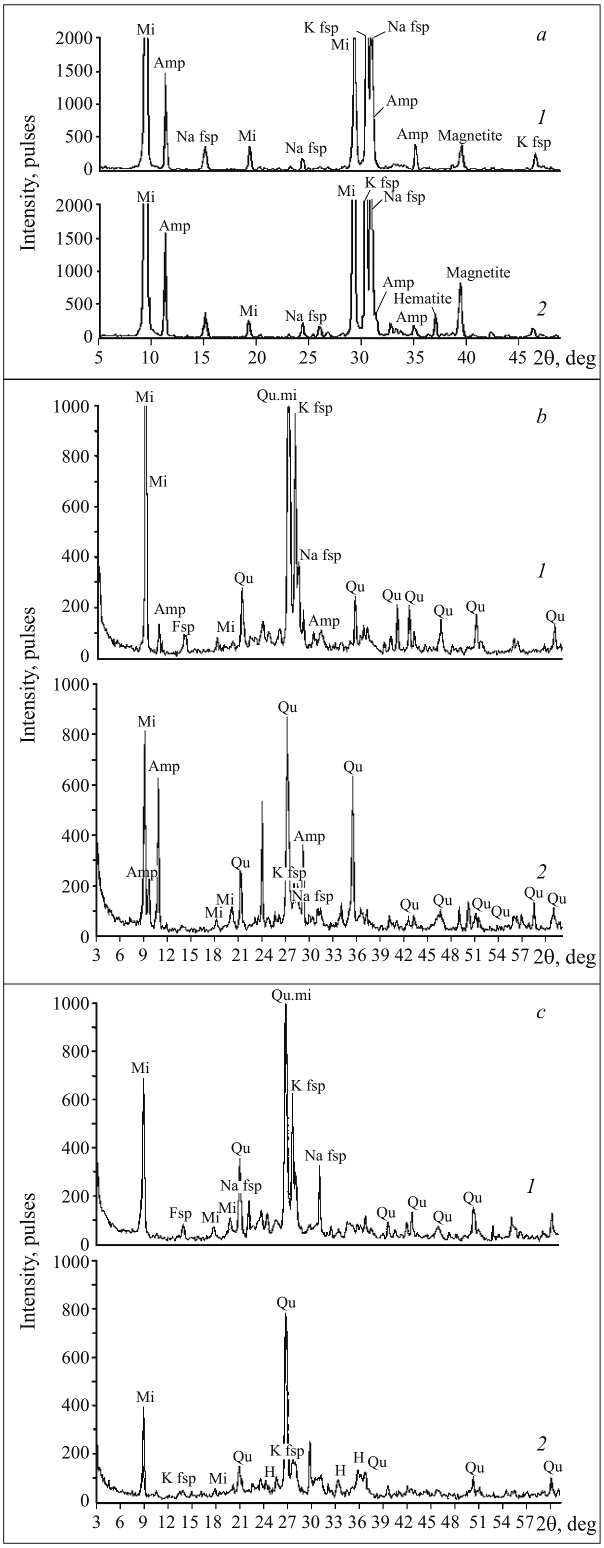

Fig. 1. Diffractograms: *a*) slurry (*1*); magnetic fraction (*2*); *b*) ceramic after firing at 950°C; *c*) at 1100°C, with slurry (*1*), with magnetic fraction (*2*).

Syenite concentration wastes (samples E-4) were used as fluxes in ceramic tile paste. Cambrian clay from the Chekalovskoe deposit, used for fabrication of facing ceramic at Nefrit-Keramika Co. (Leningrad Oblast'), was the plasticizing (clay) component. The chemical compositions of the clay, slurry, and magnetic fraction are reported in Table 1.

TABLE 2. Compositions of Ceramic Tile Pastes

Raw material	Mass content of compositions, %		
	1	2	3
Chekalovskoe clay	70	70	63
Magnetic fraction	30	–	–
Slurry	–	30	–
Quartz sand	–	–	17
Prosyanovskoe kaolin	–	–	16
Limestone	–	–	6

The mineral composition of the raw materials and ceramic was determined by x-ray phase analysis (XPA) on a DRON-3M automatic diffractometer in copper radiation with a nickel filter. The experimental data were processed with an applied software package (XRays) developed at the Institute of Steel and Alloys (Moscow). Two programs were used: Outset, for initial processing of the diffraction patterns and determination of the glass phase parameters, and Phan, for determining the phase composition.

In addition, the structure and phase composition of the ceramic was determined with a VEGA 2 LSH electron microscope with an attachment for microanalysis with magnification primarily within the limits of 150 – 1200 times, less frequently up to 2000 – 4000 times.

According to the XPA data, the slurry and magnetic fraction (Fig. 1*a*) basically consisted of sodium feldspar ($d = 3.18$; 4.02; 6.37 Å), potassium feldspar ($d = 3.24$; 2.12 Å), iron silicates (biotite $d = 10.04$; 5.04; 3.36 Å, amphibole $d = 8.42$; 2.77 Å), hematite ($d = 2.69$ Å), and magnetite ($d = 2.52$ Å). The magnetic fraction contained much more magnetite, hematite, iron silicates, and less feldspars than the slurry. This was reflected in the chemical composition of the raw material: the high iron content and low acidity of the magnetic fraction.

The mineral composition of the clay was basically represented by hydromica, as well as quartz, feldspar, and chlorite.

Experimental two-component pastes containing Cambrian clay (70%) and syenite concentration wastes (30%) were prepared for the study (Table 2). The same amount of flux in ceramic tile paste (30%) was previously established as optimum for improving the properties of the ceramics (sintering capacity, strength) made from Cambrian clay and Chupinskoe POF pegmatite dust removal wastes [3].

The experimental ceramic pastes were prepared with technology that included drying, grinding, sieving, suspension, and mixing of the components in a laboratory ball mixer to a 0.063 – 1.5% residue on the sieve. After 24-h aging, the working moisture content of the pastes was 18 – 20%. Tiles measuring 50 × 50 × 8 mm were molded

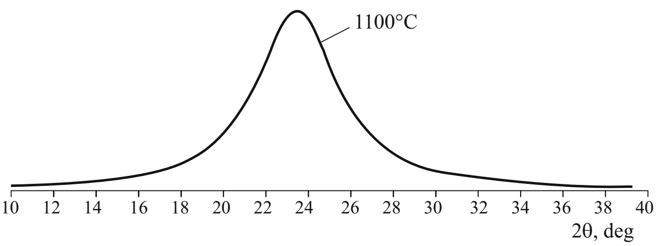

Fig. 2. Diffractogram of the glass phase in a ceramic with a magnetic fraction at 1100°C.

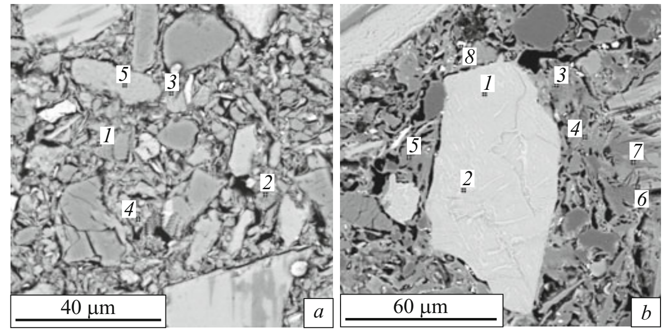

Fig. 3. Electron image of the structure of the ceramic at 1100°C: with slurry (*a*): *1*, *3*, *4*) glass phase; *2*) quartz; *5*) potassium feldspar; with magnetic fraction (*b*): *1*, *2*) amphiboles; *3*, *4*) glass phase; *5*) K-feldspar; *6*, *7*) pyroxenes; *8*) magnetite.

from the pastes. The tiles were first dried at the temperature of 105°C and then fired in a KO-14 laboratory Silit furnace at 950 – 1100°C with a 50°C interval. The samples were held in the furnace when the required temperature was attained. The samples were cooled together with the furnace.

The properties of the samples of ceramic pastes were determined according to the corresponding GOSTs: bending strength according to GOST 8462, average density, water absorption of the articles according to GOST 7025.

The mineral composition of ceramics 1 and 2 (Table 2) based on XPA data (Fig. 1*b*) at 950°C was represented by feldspars, amphibole, micas, and quartz. The chlorite line in the initial clay composition was absent on both diffractograms since it was dehydrated and the lattice was destroyed in the temperature region below 950°C. Dehydration of the chlorite and hydromica in the clay favors sintering of these ceramic pastes at 950°C.

At 1100°C, there are no amphibole lines in the diffractograms of these pastes (Fig. 1*c*), and the intensity of the quartz, mica, and feldspar lines decreases, which indicates partial transition of these minerals into the amorphous state due to formation of low-melting eutectics of ferruginous minerals (amphiboles, micas, hematite, magnetite) with other minerals in the ceramic paste (quartz, feldspars, products of decomposition of hydromicas).

A comparison of the diffractograms of the ceramic with slurry and a magnetic fraction (see Fig. 1) shows that sintering takes place more intensively in the ceramic with a magnetic fraction, due to the high content of iron silicates and iron oxides in the given raw material.

The curve showing the presence of glass phase (Fig. 2) at 1100°C was plotted for the ceramic with a magnetic fraction by corresponding calculations of the diffraction patterns with the applied software package. The glass phase did not appear in the ceramic with slurry according to the diffractogram, probably because the amount was below the limit of sensitivity of the given method.

Electron microscopy showed that the ceramic obtained after firing at 950 – 1100°C has an irregularly granular structure consisting of a fine-grained base (grains less than 5 μm in size) and disseminated deposits 10 – 50 μm in size (in the ceramic with slurry) and up to 120 μm (in the ceramic with a magnetic fraction). According to the data from the microanalysis, the disseminated deposits in the ceramic with slurry are represented by feldspar, quartz, and biotite.

In addition to the indicated minerals, the ceramic with a magnetic fraction contained individual grains of amphiboles, pyroxenes, and magnetite (Fig. 3).

Finer grains were not identified by microanalysis. At 1100°C, the same crystalline phases were present in the photomicrographs (see Fig. 3) as at 950°C, but sections of glass phase were also found between grains.

In comparison to electron microscopy, XPA identified a smaller number of crystalline phases since it only reflects the basic phases that predominate in the given material, while electron microscopy even shows individual grains. The combination of these methods allowed more completely characterizing the phase composition of the ceramic.

The glass phase is most clearly manifested in the ceramic with a magnetic fraction (see Fig. 3*b*), which is agreement with the XPA data. The chemical composition of the glass phase, determined by electron microscopy, varied within wide limits in six sections of the sample (%): 48.91 – 61.39 SiO_2; 0 – 4.17 TiO_2; 17.41 – 24.07 Al_2O_3; 4.5 – 12.44 Fe_2O_3; 4.17 – 10.01 MgO; 0.83 – 1.88 CaO; 0.99 – 1.99 Na_2O; 4.60 – 7.76 K_2O. In comparison to the initial clay, the glass phase was enriched with the aluminum, magnesium and iron oxides contained in the syenite concentration wastes. The acidity decreased with an increase in the iron content.

The inhomogeneity of the chemical composition of the glass phase is due to the irregular distribution of the magnesium iron and aluminosilicate minerals in the raw material in the ceramic.

As noted in [4], total homogenization of technogenic polymineral raw material was not attained. Local equilibria in the melt – crystalline phase system in the individual sections of the fired sample (sinter) were established when it was used in the ceramic.

Fine fractions (< 5 μm) of the clay raw material and the inhomogeneous (in composition) flux (technogenic raw material) primarily participate in formation of the glass phase.

TABLE 3. Properties of Ceramic Pastes

Index	Experimental		Industrial
	1	2	3
Shrinkage, %, at temperature, °C:			
100	3.07	6.30	6.10
900	5.00	6.40	–
950	7.00	8.20	8.93
1000	9.80	8.40	9.87
1050	11.20	8.93	10.60
1100	11.80	9.87	11.93
Water absorption, %, at temperature, °C:			
950	11.95	16.03	14.63
1050	5.96	13.67	10.20
1100	2.35	13.30	6.63
Bending strength, MPa, at temperature, °C:			
1050	29.05	23.63	29.11
1100	31.10	26.20	28.35
Density, g/cm^3, after firing at temperature, °C:			
950	2.45	2.65	–
1050	2.43	2.70	–
1100	2.49	2.67	–

Larger grains of minerals changed little at a firing temperature of 1100°C, playing the role of a filler.

The different effect of the mineral composition of the syenite wastes on the structure is also reflected in the properties of the ceramic.

The properties of the ceramic pastes (1, 2) with the investigated syenite concentration wastes and an industrial paste (3) are reported in Table 3.

As a result of studying the physicomechanical properties, we found that the total shrinkage of the tile paste with a magnetic fraction (paste 1) uniformly increases, which indicates the gradual development of a glass phase and sintering of the ceramic in the 900 – 1050°C temperature range.

Due to the lower amount of glass phase in paste 2, sintering was not uniform and took place at a higher temperature (950 – 1100°C).

In the 1050 – 1100°C range of firing temperatures, water absorption of the tiles with a magnetic fraction (paste 1) decreased sharply, to 2.35%, in comparison to this index for tiles containing slurry (paste 2), 13.67%, and the industrial tiles (paste 3) 6.63%, which indicates better sintering of the paste. With respect to water absorption, the tiles containing a magnetic fraction and Cambrian clay fired at 1100°C satisfy the requirements of GOST 6787–80 “Ceramic Tile for Floors” (maximum of 3.8%). The tiles with slurry had higher water absorption than paste 1 and the industrial paste (25% higher at 1050°C and two times higher at 1100°C), but it was within the limits of the requirements of GOST 6141–91 (under 16%) for facing tile.

The strength indexes and density are correlated with the shrinkage and water absorption data for the ceramic pastes. The ceramic containing a magnetic fraction had strength close to the industrial paste at 1050°C and higher in comparison to the ceramic with slurry (see Table 3).

A higher content of iron minerals in the magnetic fraction in comparison to slurry thus significantly enhanced glass formation and sintering of the ceramic, causing lower water absorption and higher strength.

These studies demonstrated the possibility of using Elet’-ozerskoe alkali syenite concentration wastes for production of facing ceramics, and this will promote comprehensive utilization of this deposit.

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